In Situ Spectroscopy for the Conversion of CO$_2$ to Syngas via Trireforming

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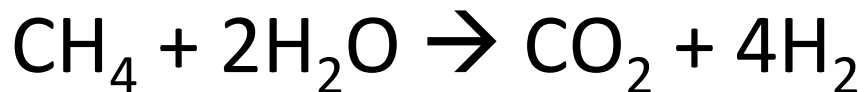ACS Fall Meeting
Philadelphia, PA
Aug 23, 2012

Introduction to CO_2 Problem

✓ 27 Texas Refineries

✓ 4.7 MM bbl/day crude

✓ ¼ Total U.S. refining
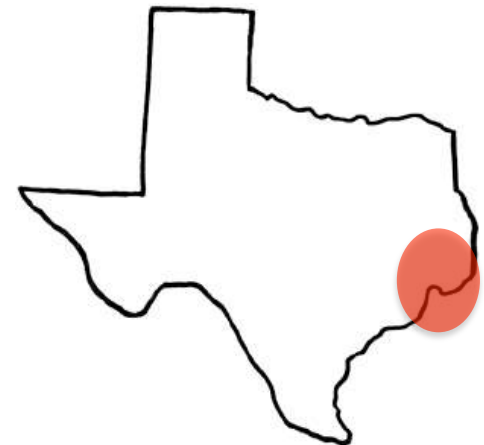
www.eia.doe.gov

✓ 500 scf H_2/bbl crude
(avg 200-800 scf/bbl)

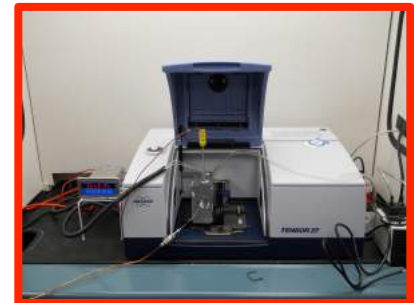$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$
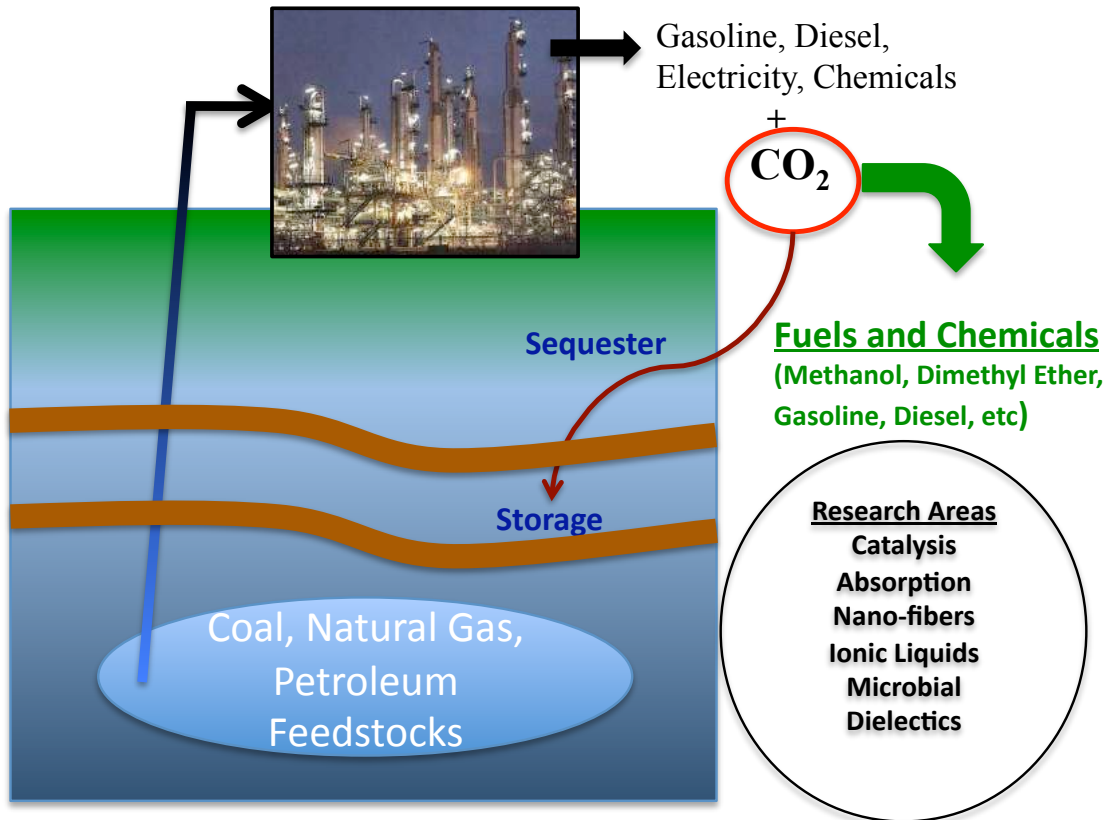
Kaiser, G.H. (2007)

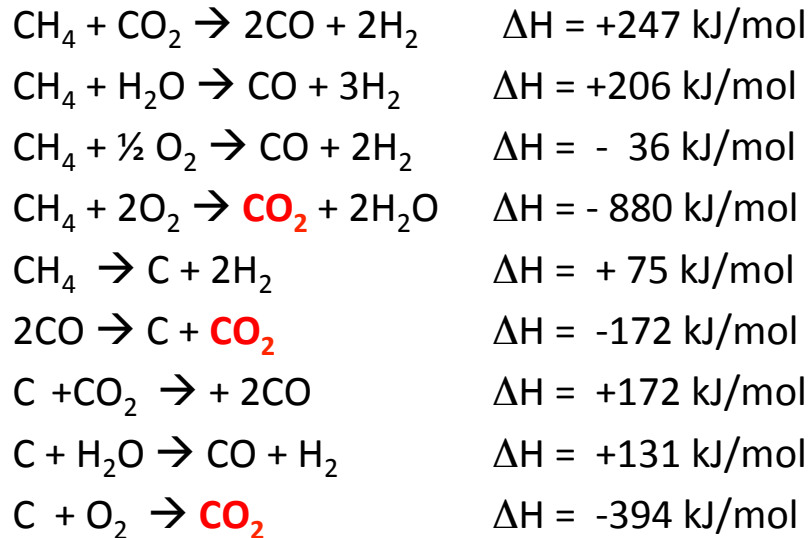**51,350 ton CO_2/day**

(18.7 MM ton/yr)

How Do We Fix the Problem?
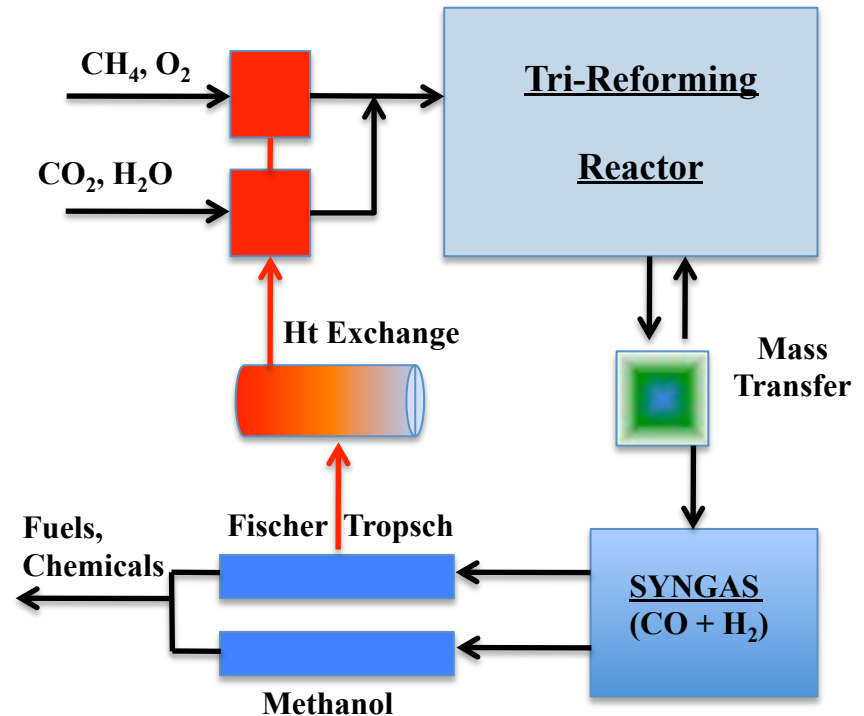
CO$_2$ Sequestration Technologies

- ✓ Capture & Store – Amine absorption, underground storage
- ✓ Dilution – decrease fossil fuels, increase biofuels
- ✓ **Conversion – CO$_2$ to usable compounds**
  (Displaces petroleum fuels)

Gasoline, Diesel, Electricity, Chemicals

+

CO$_2$

Sequester

Storage

Coal, Natural Gas, Petroleum Feedstocks

Fuels and Chemicals
(Methanol, Dimethyl Ether, Gasoline, Diesel, etc)

Research Areas
Catalysis
Absorption
Nano-fibers
Ionic Liquids
Microbial
Dielectics

Tri-Reforming: Turning CO_2 into a Fuel

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ $\qquad \Delta H = +247$ kJ/mol

$CH_4 + H_2O \rightarrow CO + 3H_2$ $\qquad \Delta H = +206$ kJ/mol

$CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2H_2$ $\qquad \Delta H = -\ 36$ kJ/mol

$CH_4 + 2O_2 \rightarrow \mathbf{CO_2} + 2H_2O$ $\qquad \Delta H = -\ 880$ kJ/mol

$CH_4 \rightarrow C + 2H_2$ $\qquad \Delta H = +\ 75$ kJ/mol

$2CO \rightarrow C + \mathbf{CO_2}$ $\qquad \Delta H = -172$ kJ/mol

$C + CO_2 \rightarrow\ + 2CO$ $\qquad \Delta H = +172$ kJ/mol

$C + H_2O \rightarrow CO + H_2$ $\qquad \Delta H = +131$ kJ/mol

$C + O_2 \rightarrow \mathbf{CO_2}$ $\qquad \Delta H = -394$ kJ/mol

Conversion: 70% CO_2, 98% CH_4
$H_2/CO = 2.0$

CH_4, O_2

CO_2, H_2O

Tri-Reforming

Reactor

Ht Exchange

Mass Transfer

Fischer Tropsch

Fuels, Chemicals

SYNGAS $(CO + H_2)$

Methanol

➤ Natural gas co-fed with reformer effluent and fresh O_2 from air
➤ Autothermal process driven by partial oxidation
➤ Catalyst development is key to success!!

Reaction Network – Thermodynamic Perspective

Rxn #	Specific Reaction	ΔH, kJ/mol	Equilibrium K @ 700°C
R1	$CH_4 + H_2O \rightarrow CO + 3H_2$	+ 206	1.78
R2	$CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2H_2$	- 36	5.13e16
R3	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	+ 247	1.43
R4	$CH_4 \rightarrow C_{(ads)} + 2H_2$	+ 75	1.51
R5	$2CO \rightarrow C_{(ads)} + CO_2$	- 172	1.06
R6	$C_{(ads)} + CO_2 \rightarrow 2CO$	+ 172	0.94
R7	$C_{(ads)} + H_2O \rightarrow CO + H_2$	+ 131	1.18
R8	$C_{(ads)} + O_2 \rightarrow CO_2$	- 394	2.11e21

✧ CO_2 producing
✧ CO_2 Converting

GOAL:

Taylor Catalyst to function @ <700°C
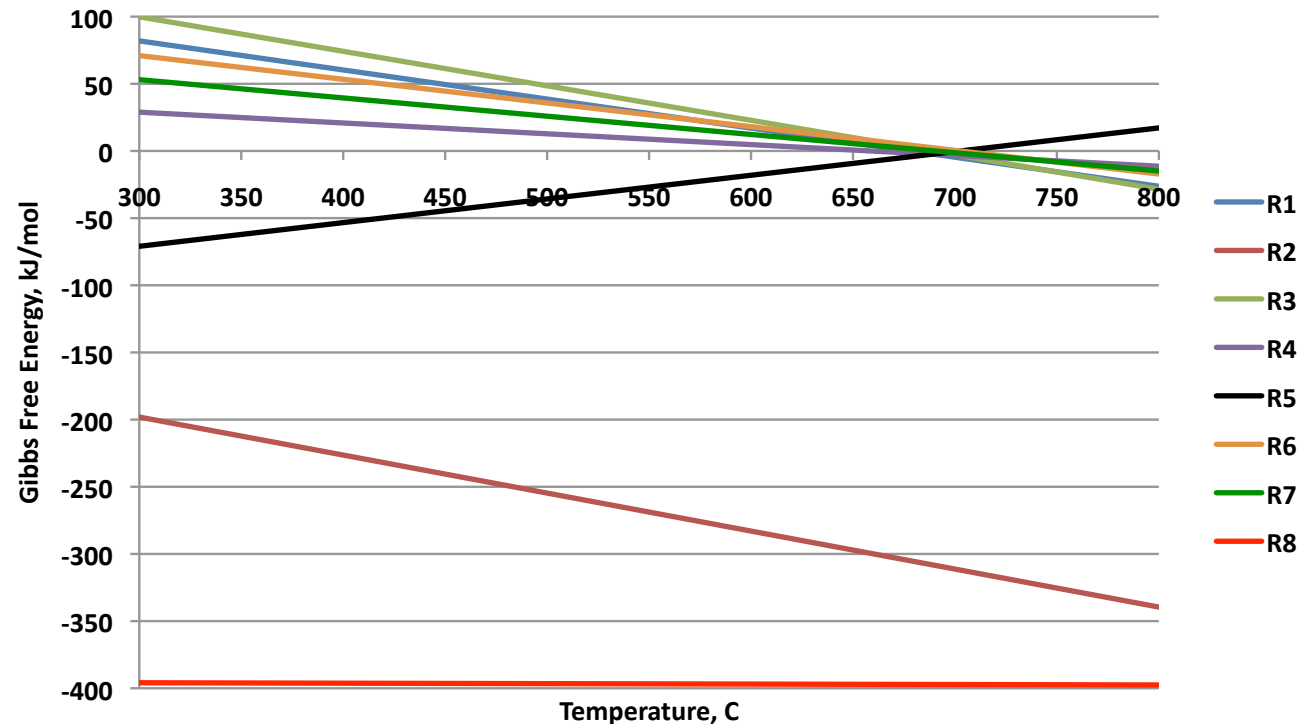
Developing Nanoparticle Catalyst

✓ **Synergism between active metal and support**

  ➤ **Oxygen vacancies within support**

  ➤ **Adsorption of carbons by active metal**

✓ **Reverse Micelles for nanoparticle formation**

  ➤ **Increased active sites per unit mass**

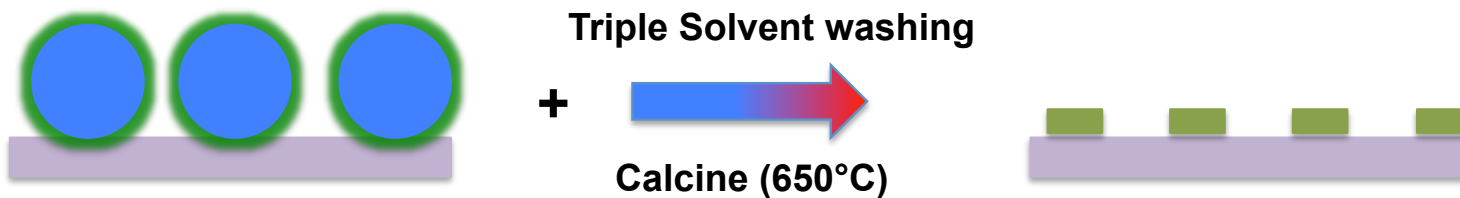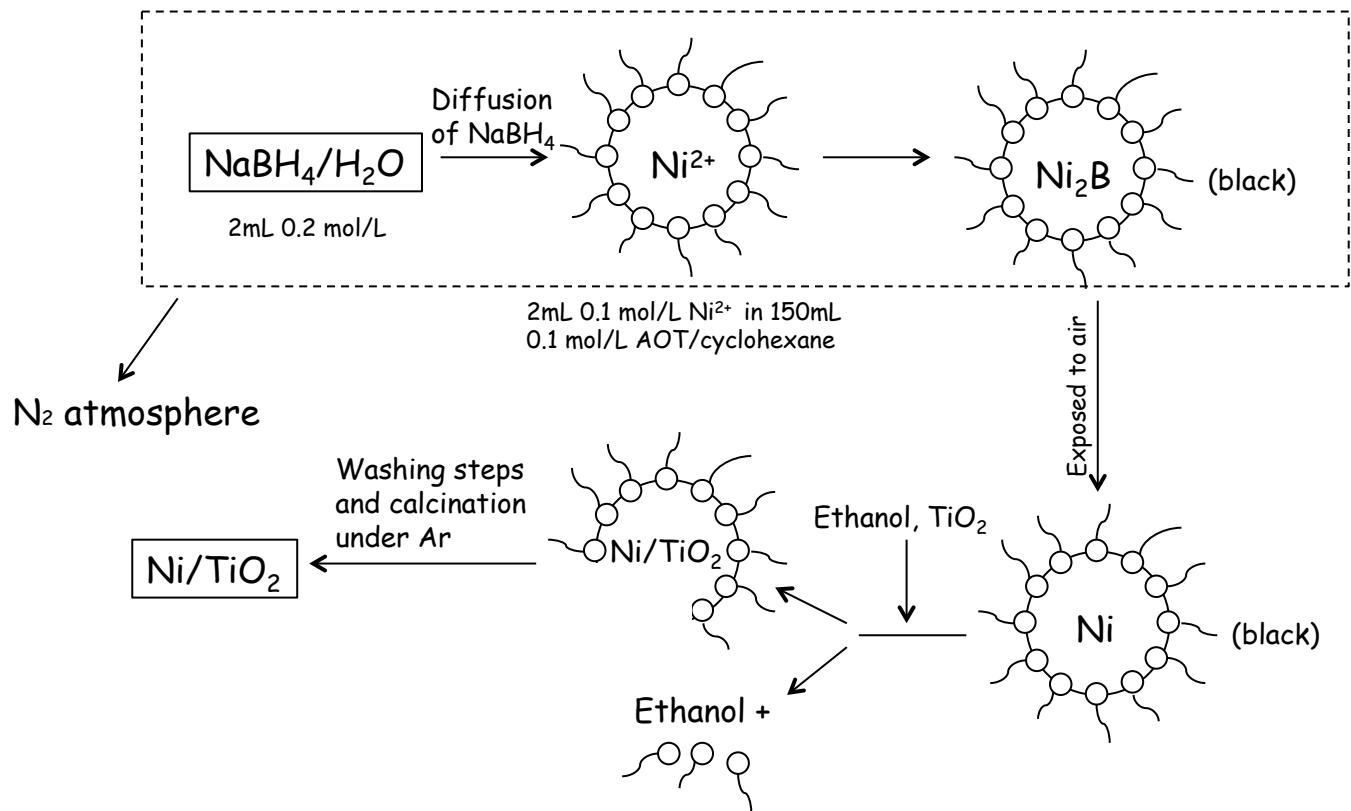 ➤ **Intimate contact between reacting species**
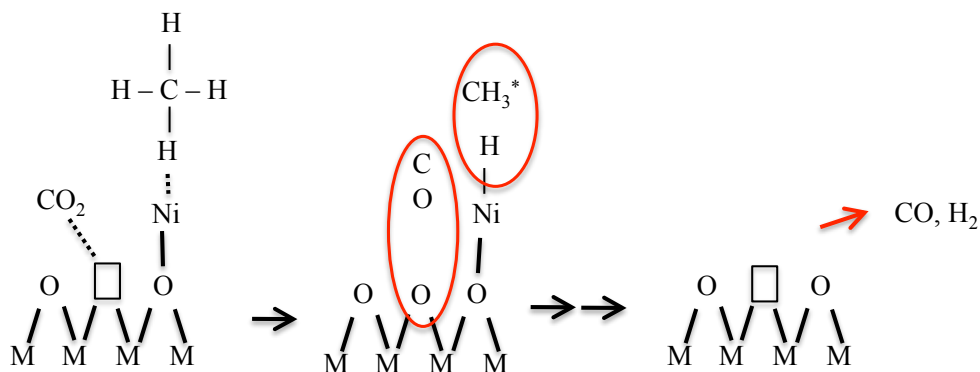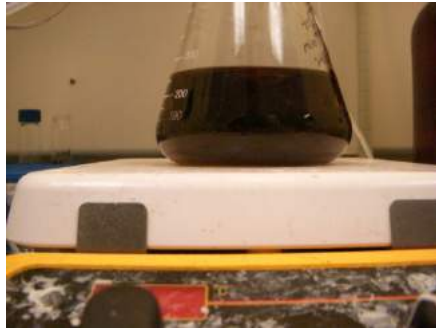
Nanoparticle Catalyst Synthesis

**Reverse Micelles
(water in oil micro-emulsions)**

Water   +   AOT
(dioctyl sodium succinate)

Cyclohexane

$Ni(NO_3)_2\ 6H_2O$

Reduce using $NaBH_4$

Complete Ni
Reverse Micelle

Ni^o
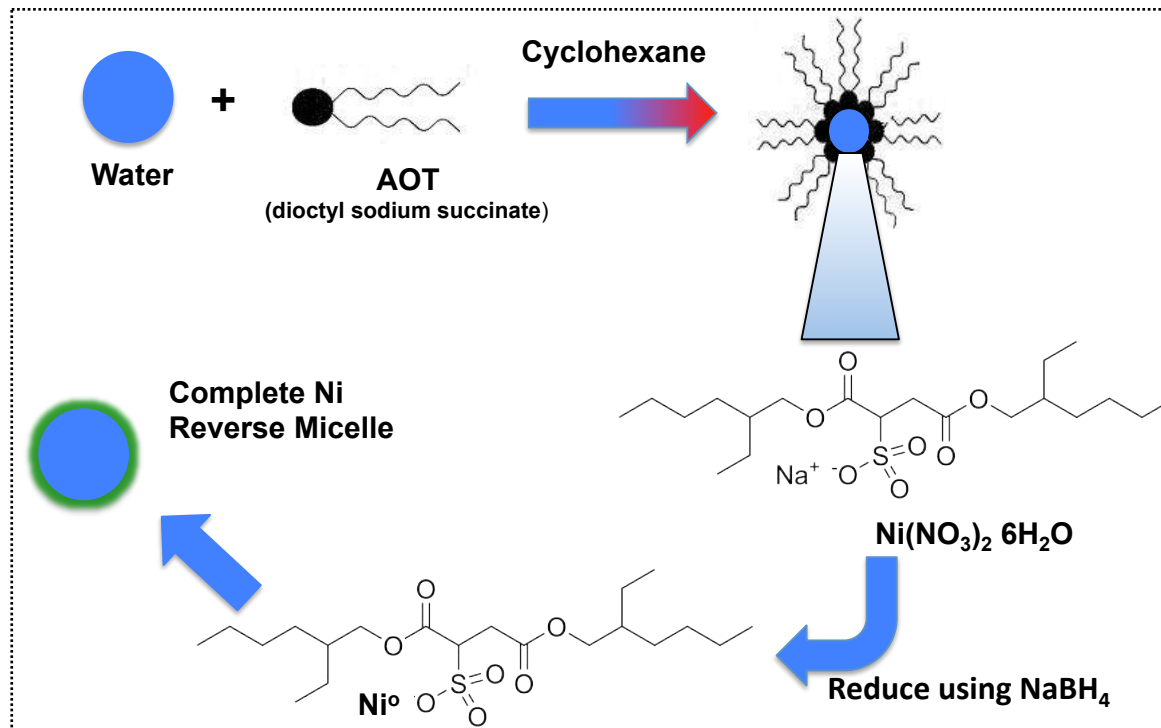
Nanoparticle Catalyst Synthesis

RM Ni$_2$B and Ni in <u>Ambient</u> Environment

60 mins   6 hrs   9 hrs   12 hrs
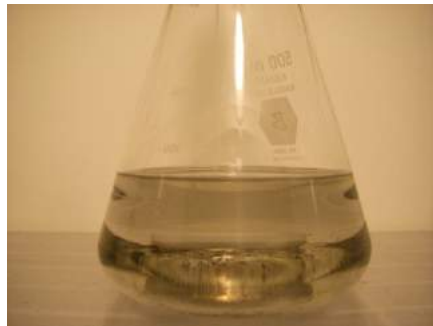
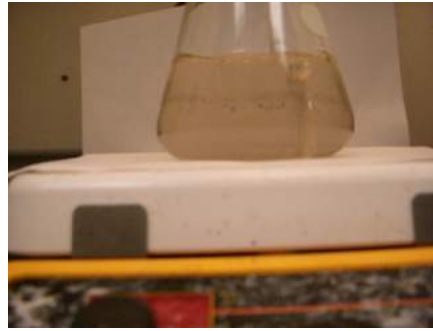15 hrs   18 hrs   21 hrs

Procedure: RM Ni^{2+} and RM solution stirred for **1 hour**

Add BH$_4^-$ solution to RM solution and stirred for **30 secs**

Mix RM Ni^{2+} and RM BH$_4^-$ solutions

Reduction of RM Ni^{2+} to RM Ni$_2$B and Ni
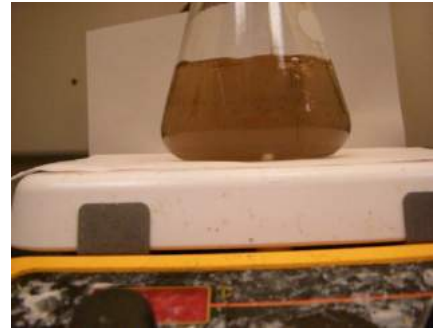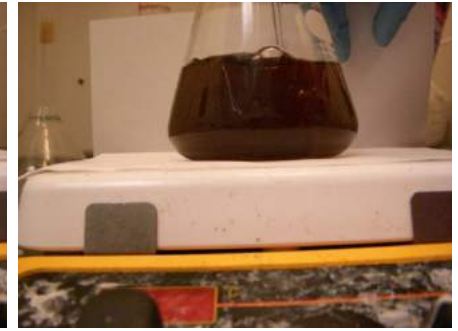
0 min   2 mins   7 mins   14 mins
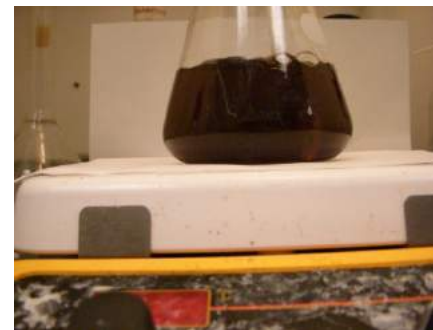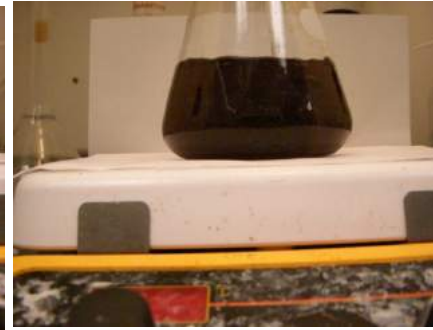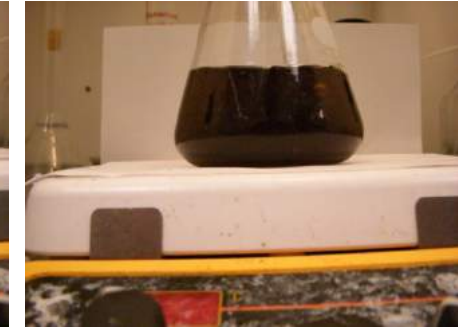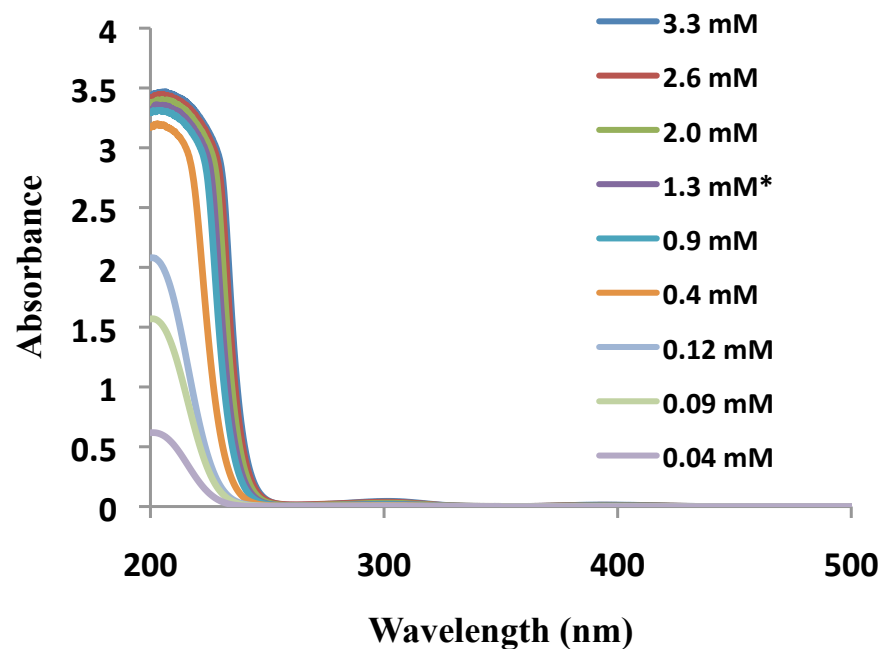

16 min   17 mins   18 mins   19 mins

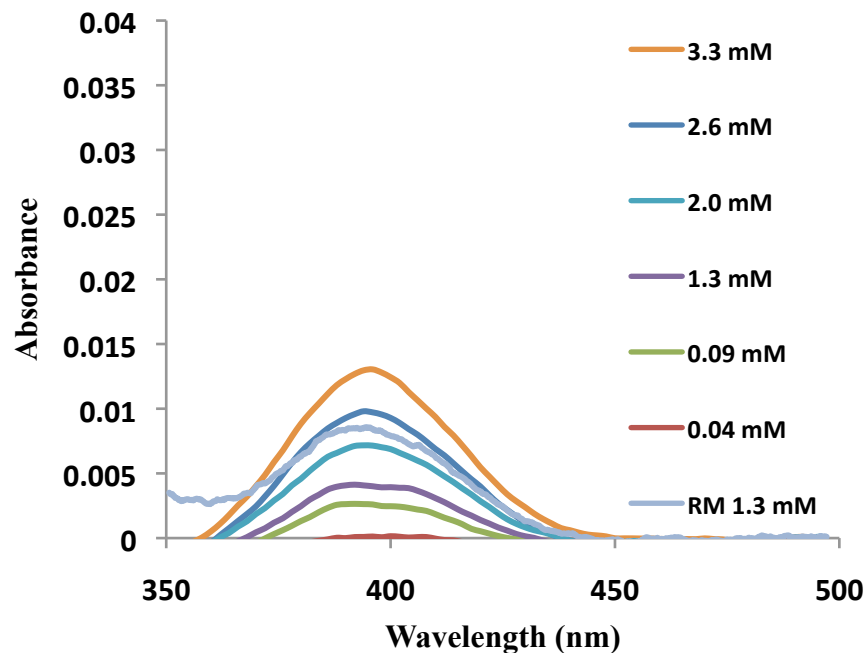Procedure: RM Ni^{2+} and RM solution stirred for **1 hour**

Add BH$_4^-$ solution to RM solution and stirred for **30 secs**

Mix RM Ni^{2+} and RM BH$_4^-$ solutions

UV-Vis of Nickel Reverse Micelle Formation
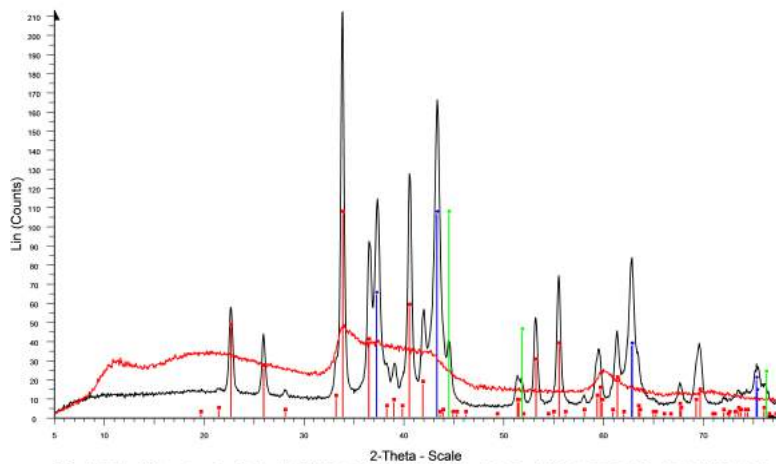

Ni(NO$_3$)$_2$ at various concentrations in aqueous solutions

Ni(NO$_3$)$_2$ at various concentrations in aqueous solutions and AOT/cyclohexane

◆ Absorption peaks at 207, 300, & 400 nm
◆ RM's (0.1 M AOT/Cyclohexane prepared with 1.3 mM Ni^{2+}
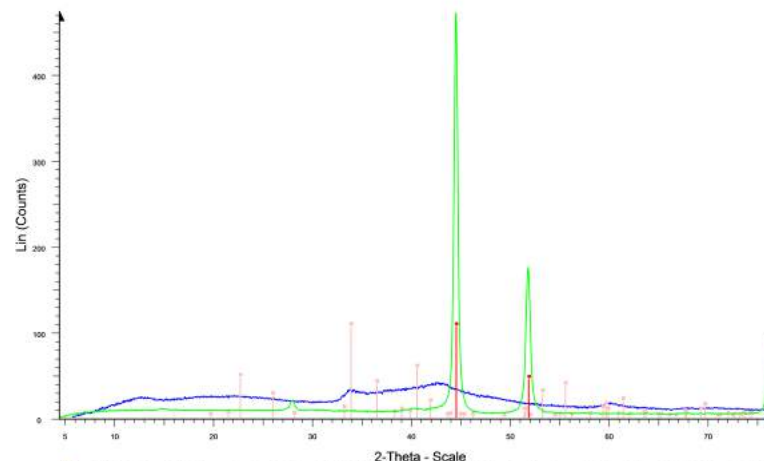◆ Calibration for Ni^{2+} can be made at the 400 nm absorption peak

XRD Analysis of RM Nickel Reduction

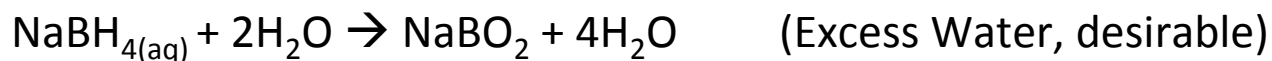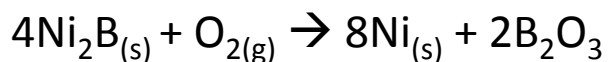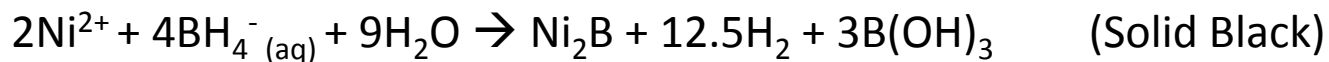Prepared with N_2 de-aerated H2O
- ✓ Before Heating
- ✓ After heating 500°C for 2 hrs

Prepared with copious de-aerated water
- ✓ Before Heating
- ✓ After heating 500°C for 2 hrs

$$2Ni^{2+} + 4BH_4^-{}_{(aq)} + 9H_2O \rightarrow Ni_2B + 12.5H_2 + 3B(OH)_3 \qquad \text{(Solid Black)}$$

$$4Ni_2B_{(s)} + O_{2(g)} \rightarrow 8Ni_{(s)} + 2B_2O_3$$

$$NaBH_{4(aq)} + 2H_2O \rightarrow NaBO_2 + 4H_2O \qquad \text{(Excess Water, desirable)}$$

?

$$Ni + NiO + BO_2^- \rightarrow Ni_3(BO_3)_2 \qquad \text{(Undesirable, Pale Green)}$$
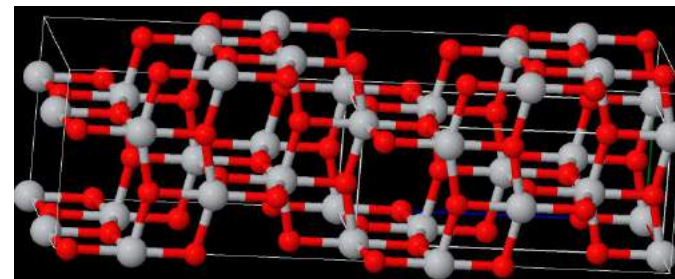
XRD results of Completed Catalyst
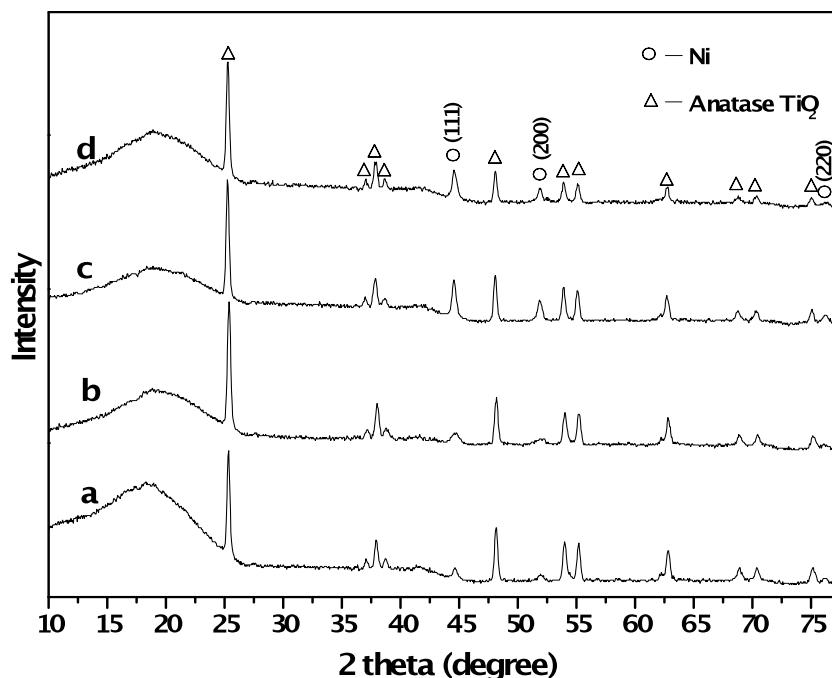
Ni Content (SEM-EDX)
(a) 5%   (7)
(b) 10% (11)
(c) 15% (13)
(d) 20% (21)

Ni Particle Sizes, nm

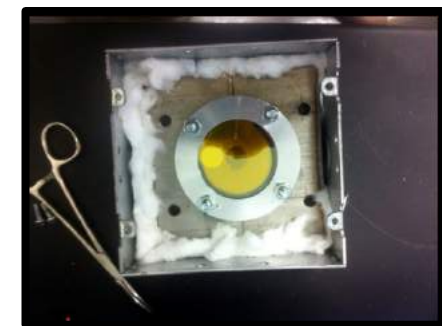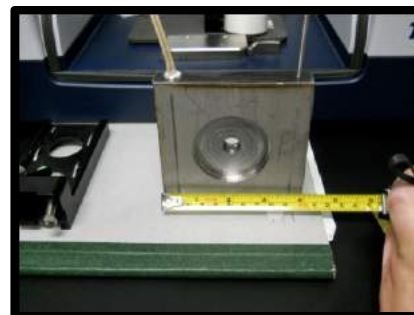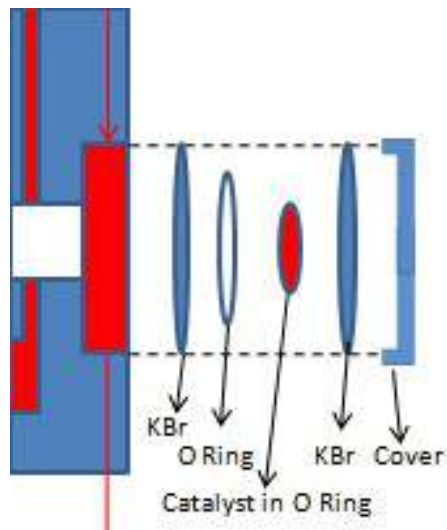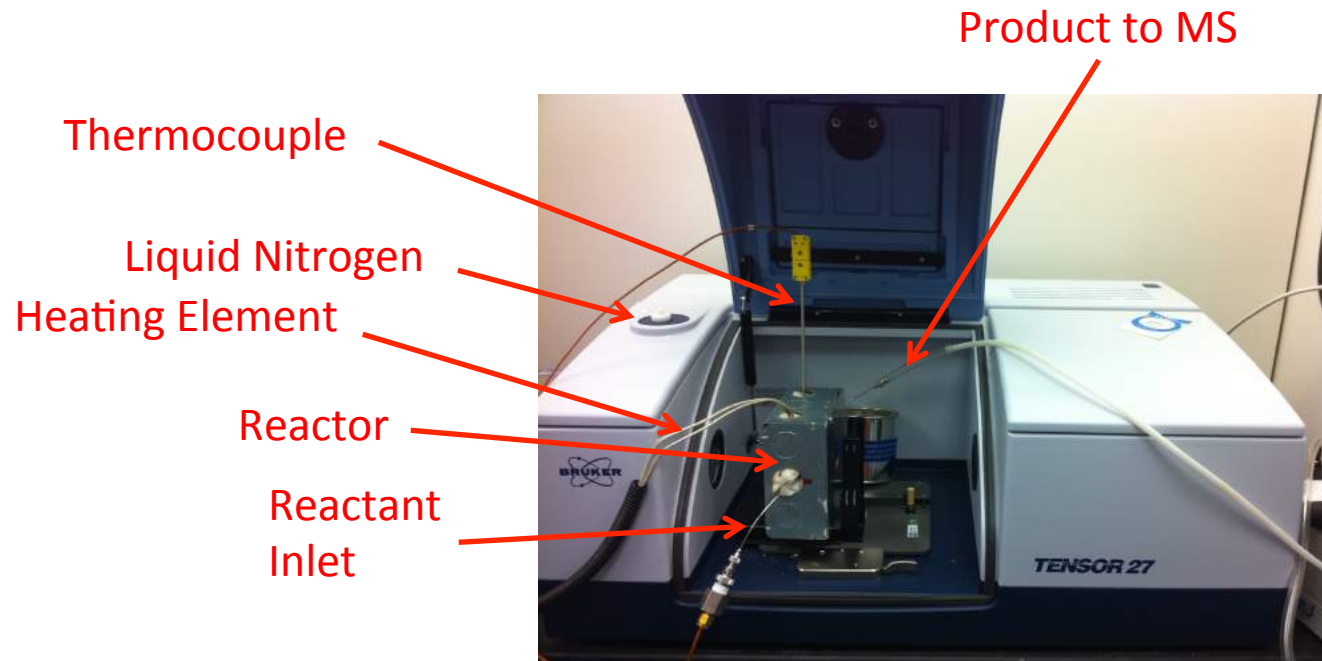| 111	200	220
16.94	19.17	24.75
11.25		17.32
23.16	19.17	19.91
18.66	21.64	24.75
AVG **17.50**	**19.99**	**21.68**
St Dev **4.92**	**1.43**	**3.70**
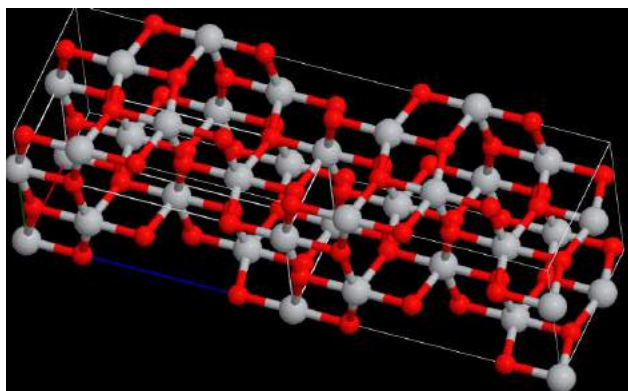
Identification of Active Sites Using Operando Spectroscopy

➤ Which are the active sites of the catalyst?

➤ How does the adsorbed gases react with the active sites?

➤ What intermediate species will be generated during the reaction and why does this happen?

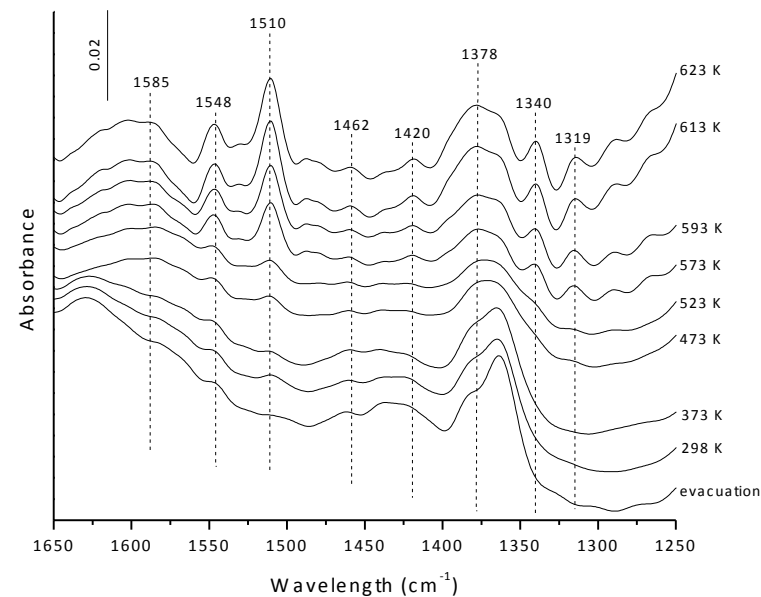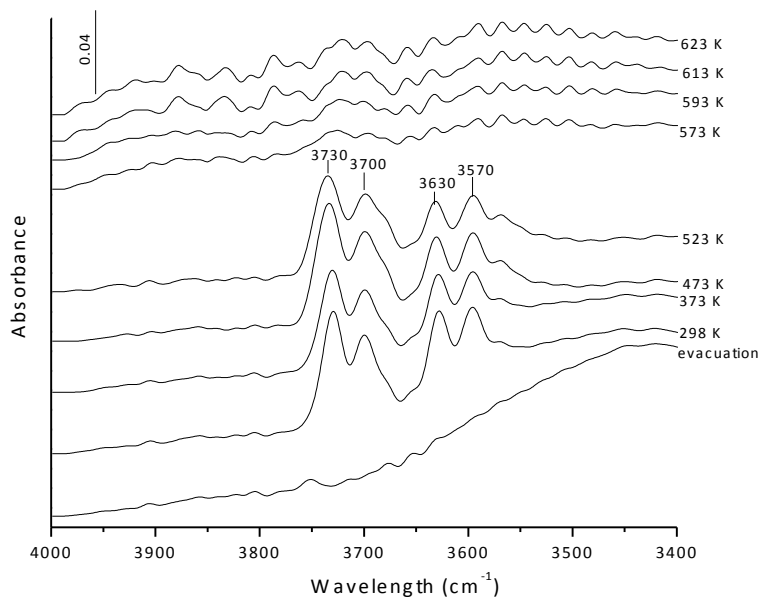➤ How can the catalyst be manipulated to increase CO_2 conversion with decreased reaction temperatures?

In situ FTIR can be a very useful tool to elucidate the complicated mechanism of a catalytic reaction

Our *In situ* FTIR System

Product to MS

Thermocouple

Liquid Nitrogen
Heating Element

Reactor

Reactant
Inlet

KBr
O Ring
KBr Cover
Catalyst in O Ring
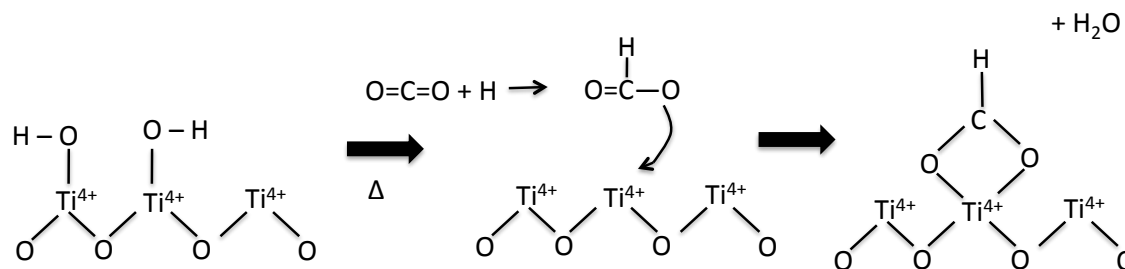
ZnSe Crystal Windows
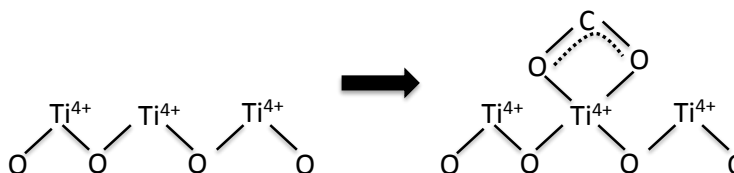
CO$_2$ adsorption on TiO$_2$

Formate (T > 300°C)

1585, 1548, 1378, 1340 cm^{-1}

Bidentate (T > 250°C)

1319 cm^{-1}

CO adsorption on TiO$_2$
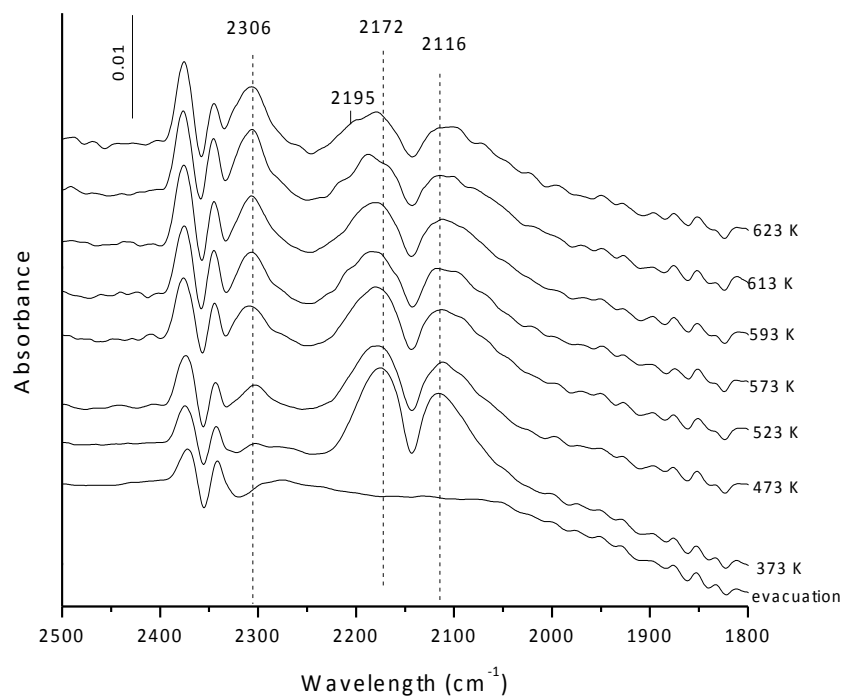
- ◆ **At higher temps 2116 cm^{-1} decreased intensity and 2172 shifts to 2180 cm^{-1}**
- ◆ **Band at 2172 cm^{-1} – Unsaturated Ti^{4+} sites**
- ◆ **Band at 2116 cm^{-1} – Ti^{3+} sites**
- ◆ **Weaker CO adsorption as temp increases and CO$_2$^{gas} (2306 cm^{-1}) more prevalent**

$$2CO \rightarrow CO_2 + C_{ads}$$

2116 cm^{-1} 2172 cm^{-1}
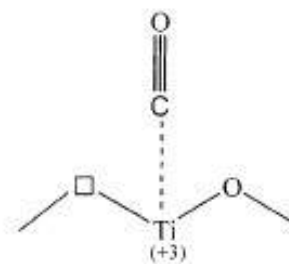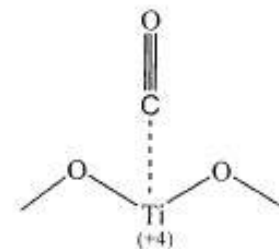
Hadjiivanov, K., J. Lamotte, and J.-C. Lavalley, Langmuir, 1997. 13(13): p. 3374-3381

CO$_2$ adsorption on Ni/TiO$_2$
(reduced in H$_2$ @ 500°C)
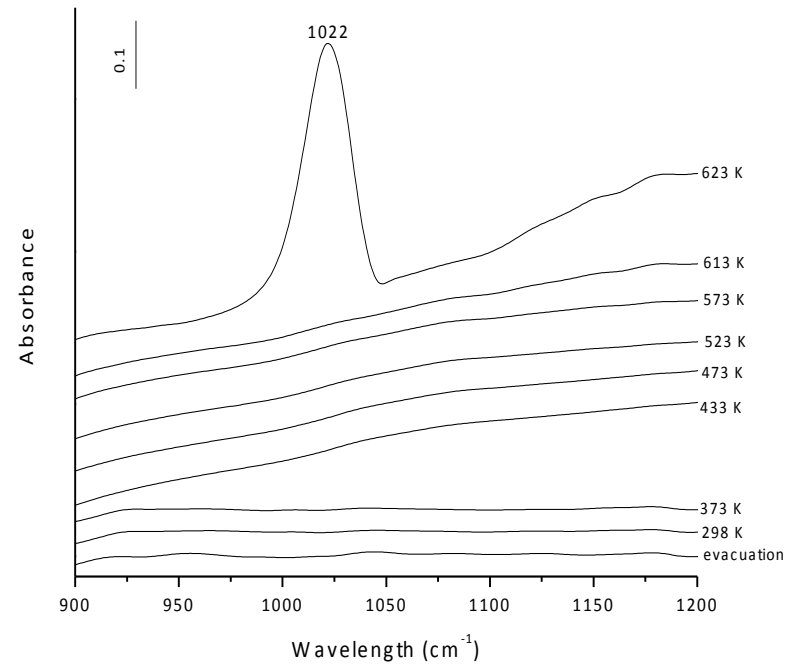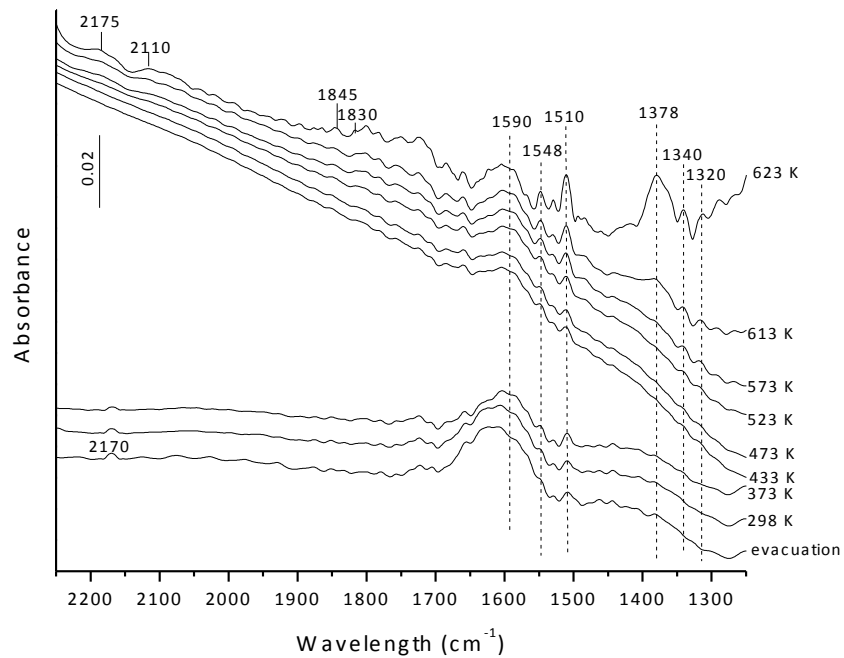
- TiO$_x$ oxidized by CO$_2$ (2170 cm^{-1})
- 1022 cm^{-1} Ti – O lattice vibration (i.e. oxygen mobility)
- 3-fold CO adsorption Ni – stretching 1815 – 1845 cm^{-1}
- Strong metal-support interaction
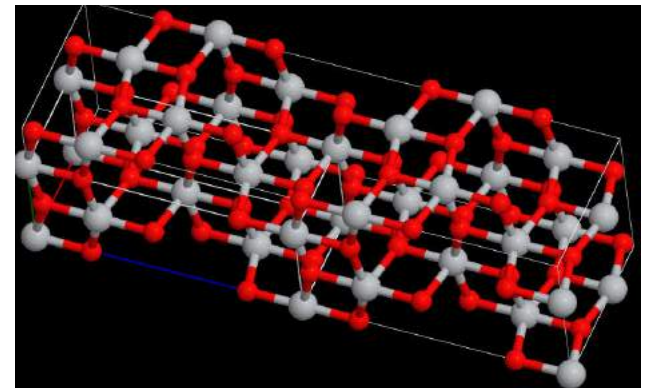
CO adsorption on Ni/TiO$_2$
(reduced in H$_2$ @ 500°C)
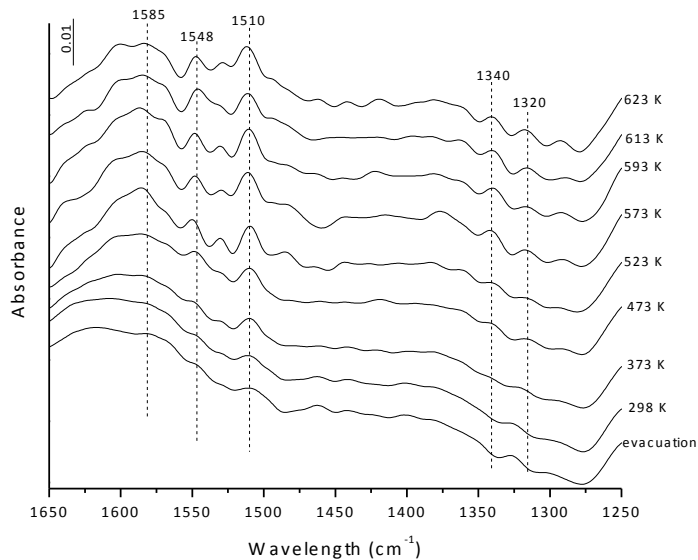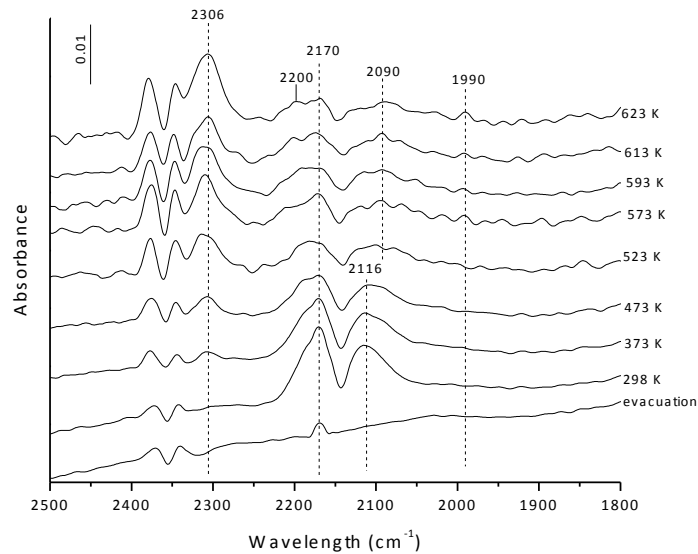
✓ Ni^0 stabilizes adsorbed C
✓ Adsorbed CO$_2$ shown by bands 1585 – 1320 cm^{-1}
✓Ni metal becomes oxidized when temperature increase
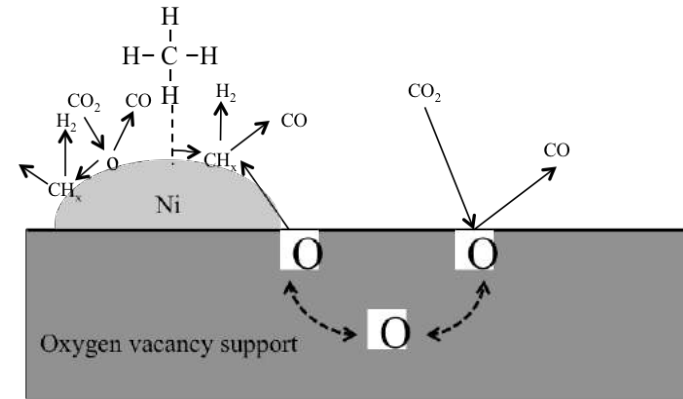
Huang, et al. (2005) Catal. Let. 105

Ni^{2+} — CO	2200 cm^{-1}
Ni^0 — CO linear	2090 cm^{-1}
OH — CO	2169 cm^{-1}
Ni^0 — CO bridged	1990 cm^{-1}
Linear CO	2040 ～ 2055 cm^{-1}

Synthesis of C-Tolerant Catalyst
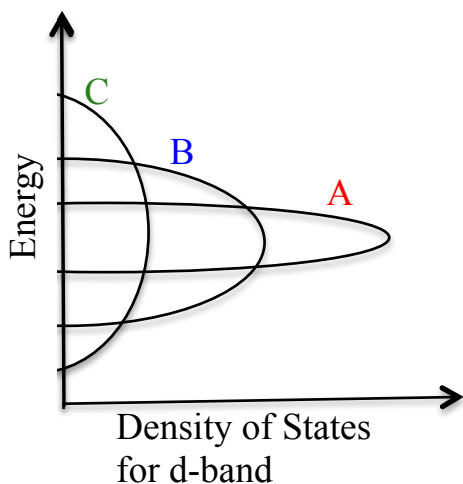
➤Catalyst tuning via co-deposition of metals
➤Overlap of d-band e$^-$ s catalyzes reverse
Boudouard reaction or gasification of carbon

$$C + CO_2 \rightarrow 2CO$$
$$C + H_2O \rightarrow CO + H_2$$
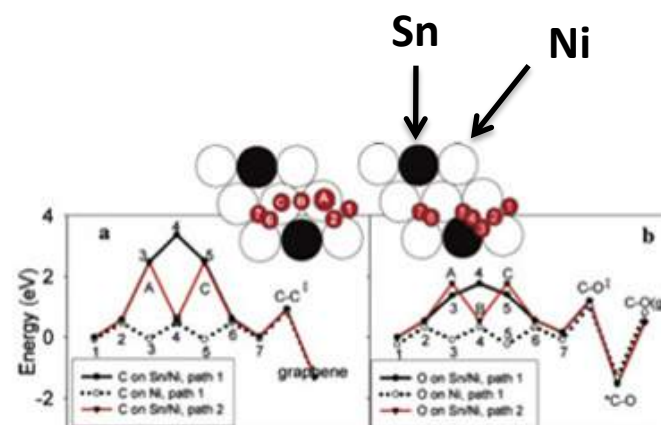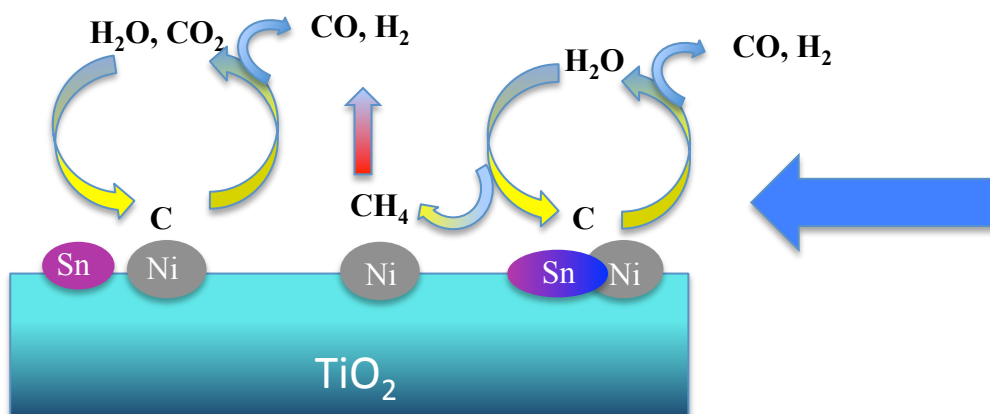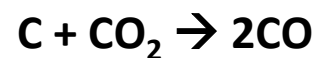
DFT modeling C-diffusion on Ni, SnNi and activation energy C-attachment at nucleation site

Nikolla et al. (2006) JACS, 128, 11355

Identification of NiSn Species on TiO$_2$

(Ni, Sn, NiSn, Ni$_3$Sn, Ni$_2$Sn$_3$)

Ni

NiSn 75:25

TEM – NiSn 75:25

Sn
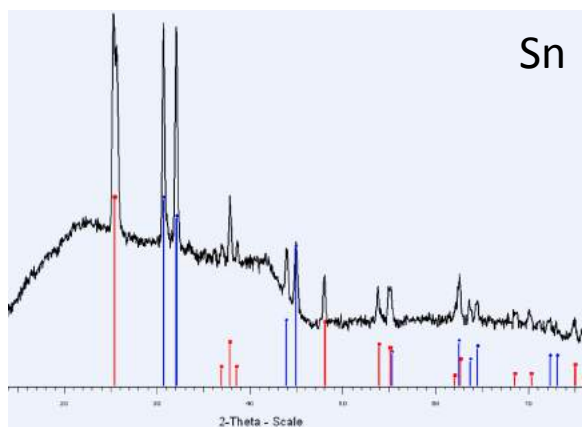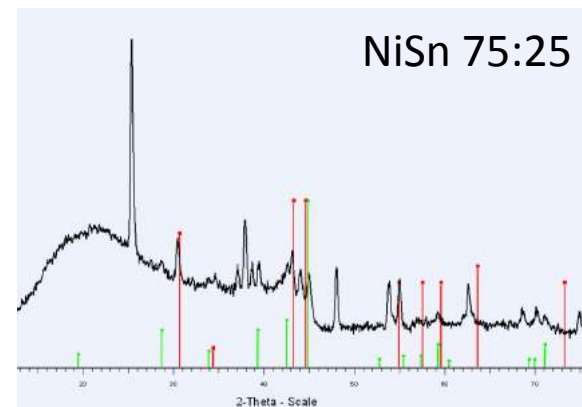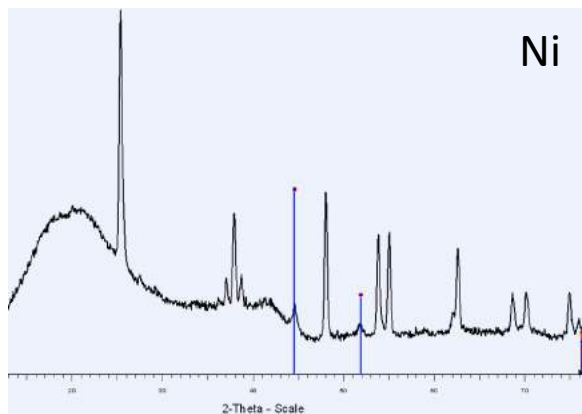
NiSn 25:75

Tri-Reforming Process Modeling
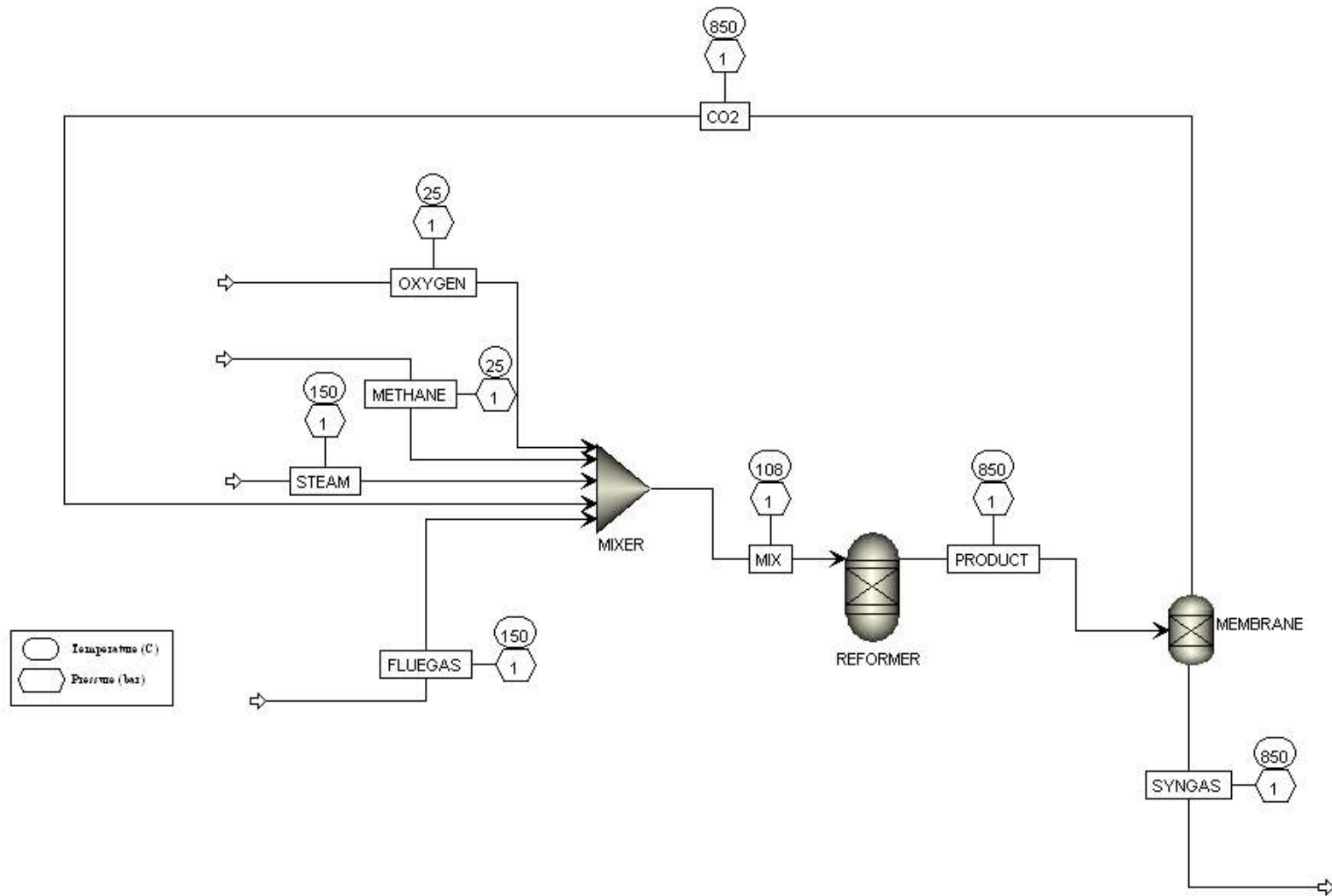
Tri-reforming Process Modeling

Assumptions:

- **Pure methane feed**

- **Flue gas enters at 150°C**

- **Reactor temperature = 850°C (96% methane conversion reported at this temperature using Ni-γAl$_2$O$_3$ catalyst [1])**

- **Aspen Plus model, R-Gibbs used for reformer- calculates equilibrium concentration based on Gibbs free energy minimization**

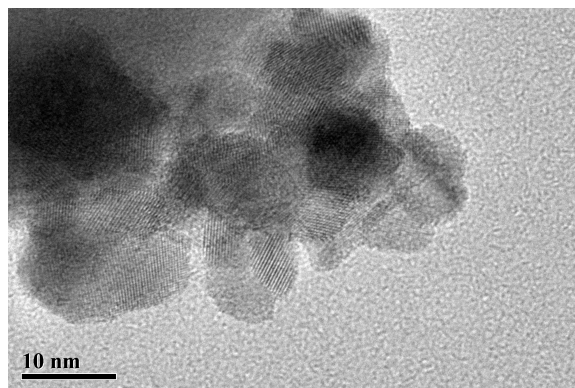- **CO$_2$ membrane modeled on MTR's Polaris™ membrane [2] : (80% CO$_2$ recovery with 95 vol% purity of CO$_2$)**

References: [1] Maciel, L., et al., *Kinetic evaluation of the tri-reforming process of methane for syngas production.* Reaction Kinetics, Mechanisms and Catalysis, 2010. 101(2): p. 407-416.
[2] MTR: CO$_2$ removal from syngas, http://www.mtrinc.com/co2_removal_from_syngas.html

Feed Stream Conditions

	FLUEGAS	METHANE	OXYGEN	STEAM	MIX
Temperature C	150	25	25	150	107.6
Pressure atm	1	1	1	1	1
Vapor Frac	1.013	1.013	1.013	1	1
Mole Flow kmol/hr	1	1	1	1	1
Mass Flow kg/hr	200	100	10	20	331
Enthalpy MMkcal/hr	5514	1604	312	360	7849
Mole Flow kmol/hr					
H_2	0	0	0	0	0
O_2	4	0	10	0	14
N_2	144	0	0	0	144
CO	0	0	0	0	0
CO_2	16	0	0	0	17.1
H_2O	36	0	0	20	56
CH_4	0	100	0	0	100
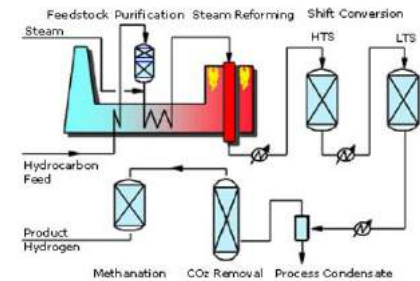
Tri-reforming Process Flow Diagram
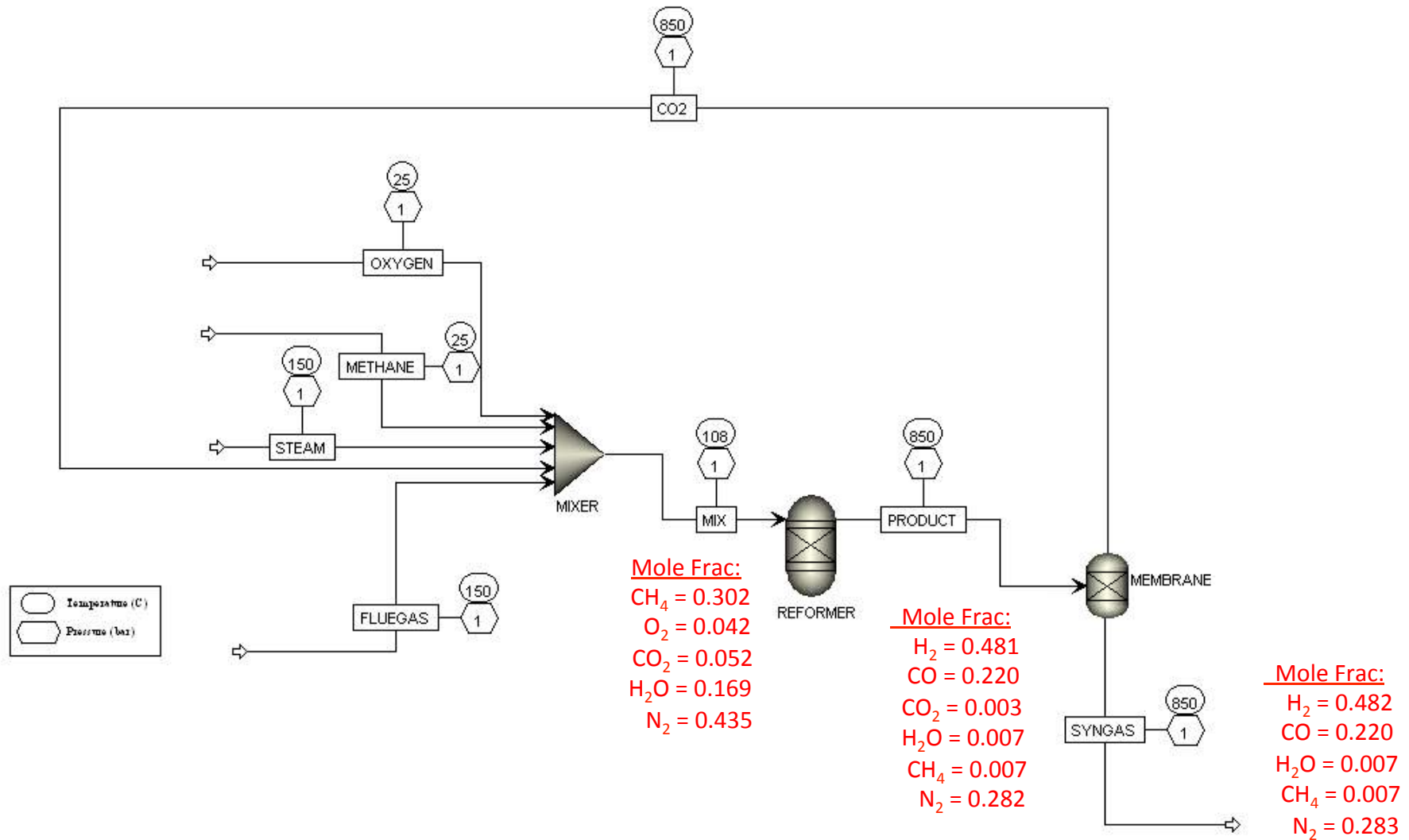
Trireforming *vs* Sequestration

Flue Gas Mol Frac
0.11 CO_2
0.22 H_2O
0.03 O_2
0.64 N_2

+ Methane → **Synthesis Gas**

2 moles   0.78 moles → 2:1 H_2/CO ΔH_{rxn} = 137 kJ/mol

1.78 moles N_2 (150 – 850°C) ΔH = 25.5 kJ/mol

Total Energy Required = 163.5 kJ/mol
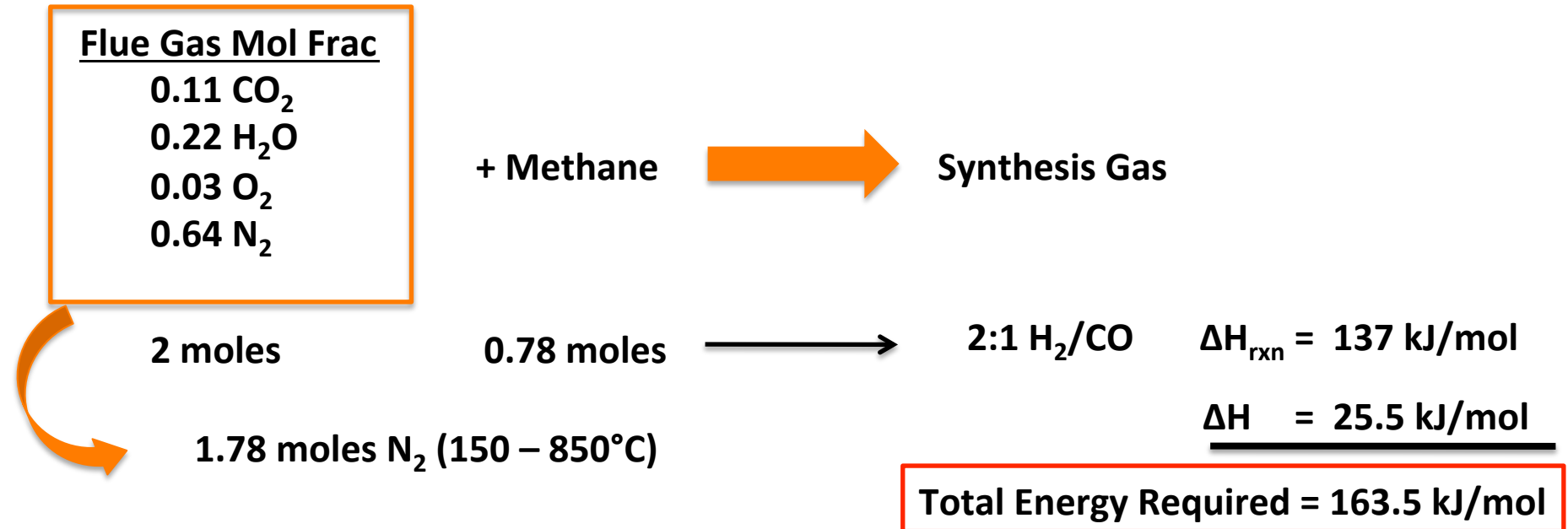
Song and Pan (2004) Catal. Today, 98, 463.

Absorption Separation:
Monoethanolomine

+

CO_2 Reforming

ΔH = 185 kJ/mol

→ **Total Energy = 345 kJ/mol**

ΔH = 160 kJ/mol

Total Energy = 302 kJ/mol

+ Pumping Costs
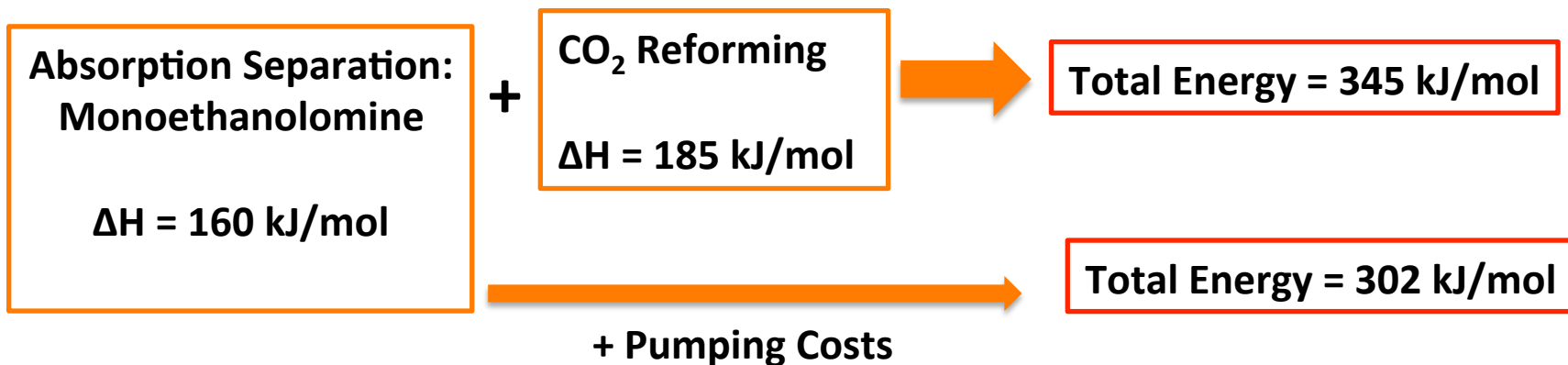
CONCLUDING REMARKS

- ❖ **Conversion CO$_2$ is difficult**
  - ➢ **Molecular stability and thermodynamics**
  - ➢ **Industrially supported if economical**
- ❖ **Thoughtful conversion strategies**
  - ➢ **Kinetically driven reactions**
  - ➢ **Membrane reactors**
- ❖ **Novel Catalyst Synthesis**
  - ➢ **Nanoparticle construction**
- ❖ **Additional Laboratory Work**
  - ➢ **Microkinetic evaluation**
  - ➢ **Catalyst design, development, & characterization**

Energy Independence Road Map

Hydrogen production
Steam-Methane Reformation

Photo-electrolysis
Biohydrogen
Electrolysis

Biomass-Gasification
Coal gasification

Autothermal
Reforming
Methane

Syngas Fischer-
Tropsch

Renewables
Solar
Wind
Biomass

Electronics

H   H

Petroleum
Fuels

Energy
Fuel Cells

Pharmaceuticals
Chemicals

H$_2$ Fuels
Combustion

ammonia
methanol
hydrogen peroxide
polymers
solvents

● **Environmentally Friendly**
● **Transitionally Necessary**
● **Traditional Hydrogen Uses**

ACKNOWLEDGEMENTS

THANK YOU

CCEE

Center for Chemical Energy Engineering

Smart Energy Laboratory

Laboratory for
Industrial Catalysis

Laboratory for
Transitional Energy Systems

Laboratory for
Fuel Cell Systems

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